PHOTOTRANSFORMATION OF PYRIDINIUM-BASED IONIC LIQUIDS IN WATER.

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Ionic liquid (ILs) are organic salts with a low melting point (<100 °C) that have been the object of several studies and industrial applications in the last years due to their unique physico-chemical properties. The low vapor pressure and flammability, the chemical and thermal stability, the high ionic conductivity, the wide electrochemical potential window and the ability to behave as catalysts make ILs useful for many applications, in particular as "green chemistry" replacements to traditional solvents. Although there is limited environmental data about these new "green solvents", the low biodegradability and considerable ecotoxicity of some of them underscore the importance to prevent ILs leakage into the environment and to develop effective means of removal and recovery from wastewaters. Taking into account the growing industrial interest and the potential threat to aquatic and terrestrial ecosystems, ILs are included in the list of the so-called "contaminants on the horizon".

In this work we compare four ILs (1-butylpyridinium bromide, BPy, 1-ethylpyridinium tetrafluoroborate, EPy, 1-(3-cyanopropyl)pyridinium chloride, CPy, and 1-butyl-4-methylpyridinium tetrafluoroborate, BMPy) by studying their overall photochemical fate and persistence by both direct and indirect photolysis. We evaluated substrate disappearance, evolution of transformation products (TPs), degree of mineralization and toxicity of the irradiated systems. The presence of different substituents, the alkyl chain length and the kind of inorganic anion influence the degradation kinetics and pathway. For instance, ~60% BPy was abated after 3 days irradiation, while only 20% EPy was removed after 7 days. The formed TPs were identified and characterized via HPLC-HRMS and, based on the overall data, a mechanism of phototransformation was proposed for the ILs examined.

Acute toxicity, evaluated with *Vibrio fischeri* bacteria, was initially very low but the phototransformation of CPy and BMPy yielded harmful compounds that caused inhibition of the bacteria luminescence. For three of the studied ILs it was possible to simulate the photochemical transformation kinetics and pathways in surface waters (direct photolysis, reaction with $^{\bullet}OH$ and with the triplet states of chromophoric dissolved organic matter), to assess their persistence in sunlit water bodies such as rivers or lakes.